

Copper(II) complexes with organic ligands. XVII. Salicylato- and cresotato-copper(II) complexes with pyridine-*N*-oxide and 2-methylpyridine-*N*-oxide

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Two modifications of salicylato-Cu(II) complex with 2-methylpyridine-*N*-oxide and *o*-, *m*-, and *p*-cresotato-Cu(II) complexes with pyridine-*N*-oxide and 2-methylpyridine-*N*-oxide were prepared. With the exception of Cu(*p*-cres)₂(pyox) (cres = cresotate anion, pyox = pyridine-*N*-oxide), all the isolated complexes have the composition Cu(R—COO)₂L₂. The assumed structure of the prepared complexes is discussed on the basis of the study of the temperature dependence of their magnetic properties and their electronic spectra in the solid state.

Были получены две модификации салицилато-Cu(II) комплекса с 2-метилпиридин-*N*-оксидом, а также *o*-, и *p*-крезотинато-Cu(II) комплексы с пиридин-*N*-оксидом и 2-метилпиридин-*N*-оксидом. Кроме соединения Cu(*n*-крез)₂(пиокс) (крез = крезотинатный анион, пиокс = пиридин-*N*-оксид), все выделенные комплексы имеют состав, отвечающий формуле Cu(R—COO)₂L₂. Структура полученных комплексов изучалась на основе зависимости их магнитных свойств от температуры, а также на основе электронных спектров в твердом состоянии.

Salicylato-copper(II) complexes of the composition Cu(sal)₂(pyox)₂ or Cu(sal)₂(quinox) (sal = salicylate anion, quinox = quinoline-*N*-oxide) with markedly different magnetic properties [1] were prepared by reactions of copper(II) salicylate tetrahydrate with pyridine-*N*-oxide and quinoline-*N*-oxide. The temperature dependence of the reciprocal value of the molar susceptibility of the magnetically diluted complex Cu(sal)₂(pyox)₂ (its effective magnetic moment $\mu_{\text{eff}}^{294\text{ K}} = 1.95$ B.M.) is typical of paramagnetism and obeys the Curie—Weiss law with the value of the Weiss constant $\Theta = 4$ K. This fact is in accordance with the assumed tetragonally distorted octahedral structure of the complex Cu(sal)₂(pyox)₂ [1]. On the other hand, the complex Cu(sal)₂(quinox) exhibits the subnormal value of its magnetic moment even at room temperature ($\mu_{\text{eff}}^{294\text{ K}} = 1.43$ B.M.) and the temperature variations of its magnetic properties are typical of antiferromagnetism [1]. It justifies to class the complex Cu(sal)₂(quinox) with the carboxylato-Cu(II) complexes of the bridged structure, typically represented by copper(II) acetate monohydrate

[2, 3]. The mentioned facts point out an important influence of the molecular ligand on the formation of the carboxylato-Cu(II) complexes with different structures.

In this work, we present the results of the preparative study of the reactions of the corresponding hydrates of Cu(II) cresotates (*o*-, *m*-, and *p*-) [4, 5] with pyridine-*N*-oxide and 2-methylpyridine-*N*-oxide (2-Mepyox) as well as the reaction of Cu(II) salicylate tetrahydrate [6] with 2-Mepyox. The structure of the prepared complexes is discussed on the basis of the study of their cryomagnetic properties as well as their electronic spectra in the solid state.

Experimental

Chemicals and instruments

The hydrates of Cu(II) salts of salicylic acid and isomeric cresotic acids used for syntheses were prepared as described in [4, 6]. Pyridine-*N*-oxide and 2-methylpyridine-*N*-oxide were prepared and purified by the method of *Ochiai* [7].

Magnetic susceptibilities were determined by the Gouy method on an apparatus of a common type described in [1].

Electronic spectra were measured on a Specord UV-VIS (Zeiss, Jena) spectrophotometer.

Powder diffractograms were obtained using Philips PW 1050 X-ray diffractometer and $\text{CuK}\alpha$ radiation.

Preparation of complexes

The salicylato-Cu(II) complex with 2-Mepyox (blue coloured modification, conventionally denoted as α) was prepared by reaction of $[\text{Cu}(\text{sal})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ with 2-Mepyox in ethanol solution at room temperature (metal—ligand ratio 1 : 4). After several weeks, the isolated complex partially changes into a green product of the same composition. This green coloured modification (conventionally denoted as β) was prepared from the mentioned starting compounds in hot acetone solution.

The preparation procedure of all the cresotato-Cu(II) complexes was similar. The starting compounds (corresponding hydrates of Cu(II) cresotates) were suspended in solutions of pyox or 2-Mepyox in organic solvents (acetone, ethanol or *n*-propanol) containing also the corresponding cresotic acid. Molar ratios in the systems were Cu(II) : L : Hcres = 1 : 4 : 0.5. The reaction systems were heated up to boiling until the solid phase dissolved. The filtered solutions were cooled down and the spontaneously crystallizing products were isolated, washed with ether, and dried in air at room temperature. The composition of the prepared complexes was determined from the content of copper (determined by chelatometry) and from the elemental analysis (C, H, N). The results are summarized in Table 1.

Magnetic measurements

Magnetic susceptibilities of the studied complexes were determined at 293, 273, 201, and 77 K. Measurements were always carried out at several intensities of magnetic field ranging from 1700 to 3700 Oe. Mercury(II) tetrathiocyanocobaltate(II) was used as a calibration substance [8]. Molar susceptibilities were corrected for the diamagnetism of the individual components using the Pascal constants [9]. Magnetic moments of the complexes of the composition $\text{Cu}(\text{R}-\text{COO})_2\text{L}_2$ were calculated from a formula

Table 1

Analytical data of the prepared complexes

Complex	Calculated/found			
	% Cu	% C	% H	% N
Cu(sal) ₂ L ₂ (2-Mepyox) ₂ α modification	11.43	56.11	4.35	5.03
	11.4	56.5	4.4	5.2
Cu(sal) ₂ (2-Mepyox) ₂ β modification	11.43	56.11	4.35	5.03
	11.3	55.7	4.45	5.1
Cu(<i>o</i> -cres) ₂ (pyox) ₂	11.43	56.11	4.35	5.03
	11.35	55.7	4.3	5.1
Cu(<i>m</i> -cres) ₂ (pyox) ₂	11.43	56.11	4.35	5.03
	11.3	55.8	4.3	4.95
Cu(<i>o</i> -cres) ₂ (2-Mepyox) ₂	10.88	57.52	4.83	4.79
	11.05	57.3	4.8	4.7
Cu(<i>m</i> -cres) ₂ (2-Mepyox) ₂	10.88	57.52	4.83	4.79
	11.0	57.5	4.9	5.0
Cu(<i>p</i> -cres) ₂ (2-Mepyox) ₂	10.88	57.52	4.83	4.79
	10.9	57.2	4.7	4.9
Cu(<i>p</i> -cres) ₂ (pyox)	13.78	54.67	4.15	3.04
	13.6	54.25	4.35	2.9

$\mu_{\text{eff}} = 2.83 [(Z'_M - N\alpha)(T + \Theta)]^{1/2}$ where the value of $N\alpha = 60 \times 10^{-6}$ cgs mol⁻¹ was substituted for the temperature independent paramagnetism of Cu²⁺ ion [10]. Values of the Weiss constant Θ were determined by a graphical extrapolation of the temperature dependence of $1/Z'_M$ to the absolute zero. Magnetic moments of the complex Cu(*p*-cres)₂(pyox) exhibiting antiferromagnetic properties were calculated as $\mu_{\text{eff}} = 2.83 [(Z'_M - N\alpha) T]^{1/2}$. The resulting values are in Table 2.

Spectral measurements

Electronic spectra of the prepared solid complexes were measured in the range of wavenumbers 13.2–30 kK using the nujol suspensions technique. The observed positions of the absorption bands are given in Table 2.

Results and discussion

Hydrates of the copper(II) salts of salicylic acid and isomeric cresotic acids used as the starting substances for the preparation of the studied carboxylato-Cu(II) complexes with pyox and 2-Mepyox represent two different structural types of Cu(II) complexes. While [Cu(sal)₂(H₂O)₂] · 2H₂O and [Cu(*m*-cres)₂(H₂O)₂] · 2H₂O belong to a group of magnetically diluted distorted octahedral Cu(II) complexes [4, 5, 11–13], the compounds [Cu₂(*o*-cres)₄(H₂O)₂] · H₂O and [Cu₂(*p*-cres)₄(H₂O)₂] ·

Table 2

Magnetic and spectral properties of the prepared complexes

Complex	Magnetic properties				Electronic spectra kK	
	T/K	$\chi'_M \cdot 10^3$	μ_{eff} B.M.	Θ/K	Band I	Band II
Cu(sal) ₂ (2-Mepyox) ₂ α modification	293	1614	1.94		14.54	
	273	1731	1.94			
	201	2287	1.93	8	≈ 12.9 sh	≈ 26.0 sh
	77	5567	1.94			
Cu(sal) ₂ (2-Mepyox) ₂ β modification	293	1619	1.94			
	273	1714	1.93	9	12.95	≈ 26.0 sh
	201	2303	1.94			
	77	5589	1.95			
Cu(o-cres) ₂ (pyox) ₂	293	1555	1.92			
	273	1699	1.95			
	201	2205	1.93	16	14.42	≈ 26.5 sh
	77	5207	1.95			
Cu(o-cres) ₂ (2-Mepyox) ₂	293	1582	1.94			
	273	1722	1.96	16	15.63	≈ 26.0 sh
	201	2248	1.95			
	77	5215	1.96		≈ 13.1 sh	
Cu(m-cres) ₂ (pyox) ₂	293	1560	1.92			
	273	1644	1.91	14	14.76	≈ 26.5 sh
	201	2211	1.92			
	77	5262	1.94			
Cu(m-cres) ₂ (2-Mepyox) ₂	293	1582	1.95			
	273	1721	1.97		15.64	≈ 26.0 sh
	201	2213	1.94	18		
	77	5064	1.95		≈ 13.1 sh	
Cu(p-cres) ₂ (2-Mepyox) ₂	293	1664	1.96			
	273	1781	1.96	6	15.16	≈ 26.0 sh
	201	2388	1.96			
	77	5916	1.97		≈ 12.9 sh	
Cu(p-cres) ₂ (pyox)	293	851	1.37			
	273	878	1.34		13.97	≈ 24.5 sh
	201	823	1.11			≈ 26.7 sh
	77	95	0.15			

$\cdot 2\text{H}_2\text{O}$ can be classed with binuclear carboxylato-Cu(II) complexes of the bridged structure [4, 5]. Reactions of these starting compounds with pyox or 2-Mepyox resulted, with the exception of Cu(*p*-cres)₂(pyox), in the complexes of the composition Cu(R-COO)₂L₂ (L is pyox or 2-Mepyox) with similar magnetic properties and the character of their electronic spectra. All the isolated complexes of this composition belong to the magnetically diluted Cu(II) complexes of which magnetic moments ($\mu_{\text{eff}}^{293\text{ K}} = 1.92\text{--}1.96$ B.M.) exceed the "spin-only" value of Cu²⁺ ion owing to the similar values of their orbital contributions. Values of magnetic suscep-

tibilities of these complexes depend on temperature in a way typical of paramagnetism while their effective magnetic moments are practically temperature independent (Table 2). The dependence of their $1/\chi_M'$ on T is linear, thus satisfying the Curie-Weiss law with positive values of the Weiss constants $\Theta = 6-18$ K (Table 2).

With respect to the position and shape of the band (in the measured region), there are two types of electronic spectra of the complexes $\text{Cu}(\text{R}-\text{COO})_2\text{L}_2$. The cresotato-Cu(II) complexes with 2-Mepyox as L and the blue coloured α modification of $\text{Cu}(\text{sal})_2(2\text{-Mepyox})_2$ may be placed into the first group. A broad absorption band of the ligand field of these complexes has its maximum located in the range of wavenumbers $\tilde{\nu} = 14.54-15.64$ kK (Table 2) and a markedly developed shoulder on the lower energy side ($\tilde{\nu}_{\text{sh}} \approx 12.9-13.1$ kK). Then green coloured β modification of $\text{Cu}(\text{sal})_2(2\text{-Mepyox})_2$ and *o*-, *m*-cresotato-Cu(II) complexes with pyox show a narrower and more intensive band of the ligand field. The position of the maxima are shifted towards lower energies ($\tilde{\nu}_{\text{max}} = 12.95-14.76$ kK; Table 2) in comparison with a corresponding complex of the first group (α modification of $\text{Cu}(\text{sal})_2(2\text{-Mepyox})_2$ and cresotato-Cu(II) complexes with 2-Mepyox). No shoulder was observed on the lower energy side of the ligand field band in the measured region. In the spectra of both groups of $\text{Cu}(\text{R}-\text{COO})_2\text{L}_2$ complexes another intensive band is seen as a shoulder at $\tilde{\nu} \approx 26.0-26.5$ kK. This band is obviously connected with some kind of a common mechanism of the metal-ligand charge transfer since it cannot be assigned to the spin-spin interaction in connection with magnetic properties of the studied complexes.

The magnetic and spectral properties of the studied group of $\text{Cu}(\text{R}-\text{COO})_2\text{L}_2$ complexes are therefore in good agreement with their assumed distorted octahedral structure, *i.e.* the coordination of Cu^{2+} ions with six oxygen atoms. It means that

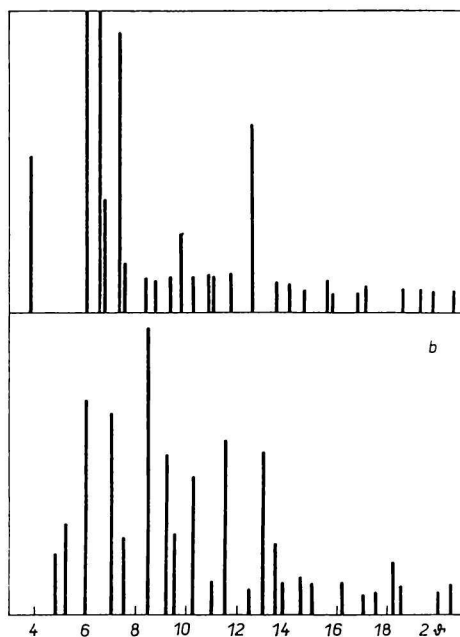


Fig. 1. X-Ray powder diffractograms of $\text{Cu}(\text{sal})_2(2\text{-Mepyox})_2$.

a) α Modification; b) β modification.

in these compounds two R—COO⁻ ions and two L molecules are planary bonded to Cu²⁺ ion (probably in *trans* configuration). The fifth and sixth coordination sites may be saturated either within the same complex molecule *e.g.* by the second oxygen of the carboxylic group, as it was found in bis(hydrogenphthalatoaquo)-Cu(II) complex [14], or by a suitable donor oxygen from a neighbouring unit of the crystal structure. Assuming the tetragonal symmetry of the studied complexes, we may assign *e.g.* the maximum of the ligand field band (the first group of complexes) to the confluent absorption of the transitions 2E_g , ${}^2B_{2g} \leftarrow {}^2B_{1g}$ and the shoulder on the lower energy side to an absorption band connected with the transition ${}^2A_{1g} \leftarrow {}^2B_{1g}$. The red shift seen in the position of the ligand field band of the second group of complexes, in comparison with those in the first group, is obviously connected with lowering of the tetragonal distortion, eventually with lowering of the ligand field strength affecting the Cu²⁺ ion in these complexes (in plane).

An interesting case in the studied group is a pair of modifications of the complex Cu(sal)₂(2-Mepyox)₂. The modifications differ markedly in the character of their X-ray powder diffractograms (positions and intensities of the diffraction maxima; Fig. 1) as well as in their colour (different character of their electronic spectra). On the other hand, their magnetic properties are mutually very alike. We may therefore assume marked differences between α and β modifications of the complex Cu(sal)₂(2-Mepyox)₂ at first in the secondary sphere, *i.e.* in their crystal structure. These differences also affect the symmetry of the coordination polyhedron (differences in electronic spectra) though their magnetic properties are similar. The isolated modifications of Cu(sal)₂(2-Mepyox)₂ may be therefore regarded as another case of the "distortion isomerism" of Cu(II) complexes [15].

In the studied series, only the complex Cu(*p*-cres)₂(pyox) differs from the preceding complexes of the type Cu(R—COO)₂L₂ not only in its composition but also in its magnetic properties. The found anomalously low value of its magnetic moment ($\mu_{\text{eff}}^{293} K = 1.37$ B.M.) points to a strong magnetic interaction between two neighbouring Cu(II) atoms in its structural unit. The temperature dependence of its magnetic susceptibility is typical of antiferromagnetism and follows the singlet—triplet eqn (*J*), derived for a system of two mutually interacting spins $S_1 = S_2 = 1/2$ [16, 17]

$$\chi'_M = \frac{g^2 N_A \beta^2}{3kT} \frac{1}{1 + 1/3 \exp(2J/kT)} + N\alpha. \quad (1)$$

Table 3

Values of $|2J|$ and T_N of the complex Cu(*p*-cres)₂(pyox)

T/K	$ 2J $		T_N/K
	cm ⁻¹	kcal mol ⁻¹	
293	310	0.88	279
273	300	0.86	270
201	298	0.85	268
Mean value	303	0.87	278

Values of the separation energy between the singlet and triplet level, $|2J|$, were calculated from eqn (1) for 293, 273, and 201 K (Table 3).

The calculated mean value of $|2J| = 303 \text{ cm}^{-1}$ does not include the value for 77 K with respect to the increased inaccuracy of the measurement owing to a very low value of the susceptibility at that temperature. The temperature T_N corresponding to the maximum susceptibility was calculated from the relationship $|2J| = 8/5 kT_N$. Curves of the dependences of χ'_M or μ_{eff} on T (Fig. 2) were computed on the basis of eqn (1) where $g = 2.16$ (value for Cu(II) acetate monohydrate) was substituted for the spectroscopic splitting factor and for $|2J|$ the above calculated mean value.

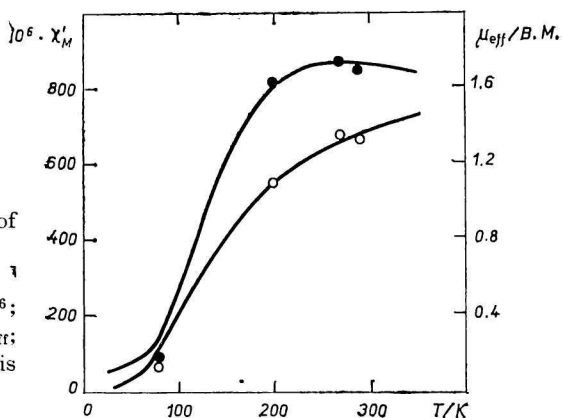


Fig. 2. Temperature dependences of $\chi'_M \cdot 10^6$ and μ_{eff} for the complex $\text{Cu}(p\text{-cres})_2(\text{pyox})$.
 ● Experimental values of $\chi'_M \cdot 10^6$;
 ○ experimental values of μ_{eff} ;
 — computed values on the basis of eqn (1).

The found data justify a conclusion that the complex $\text{Cu}(p\text{-cres})_2(\text{pyox})$ belongs to binuclear carboxylato-Cu(II) complexes of the bridged type, analogously to $\text{Cu}(\text{sal})_2(\text{quinox})$ [1]. In the binuclear $\text{Cu}_2(p\text{-cres})_4(\text{pyox})_2$ units, the *p*-cresotate ions are obviously bonded as bridges between two Cu^{2+} ions and the molecules of pyridine-*N*-oxide as neutral ligands in the axial terminal positions of the binuclear structural unit.

In conformity with the assumed structure, the electronic spectrum of the complex $\text{Cu}(p\text{-cres})_2(\text{pyox})$ shows the ligand field band with a maximum at $\tilde{\nu} = 13.97 \text{ kK}$, thus in a common position for binuclear carboxylato-Cu(II) complexes with *O*-donor molecular ligands in the axial terminal positions. The significant band assigned to the spin-spin interaction is seen in the spectrum of this complex as a shoulder at $\tilde{\nu}_{\text{sh}} \approx 26.7 \text{ kK}$. Another band manifested as a shoulder at $\tilde{\nu}_{\text{sh}} \approx 24.5 \text{ kK}$ is probably the ligand-metal charge-transfer band of a common type.

We may summarize that under the used preparative conditions the entrance of pyox or 2-Mepyox into the inner coordination sphere of salicylato-Cu(II) and cresotato-Cu(II) complexes promotes a preferential formation of the mononuclear structures with tetragonal symmetry, regardless of the mono- or binuclear nature of the starting carboxylatoquo-Cu(II) complexes. This fact can be seen in connection with a mutual influence of anionic as well as molecular ligands upon the formation of carboxylato-Cu(II) complexes of different structures, discussed in our previous works [18, 19].

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